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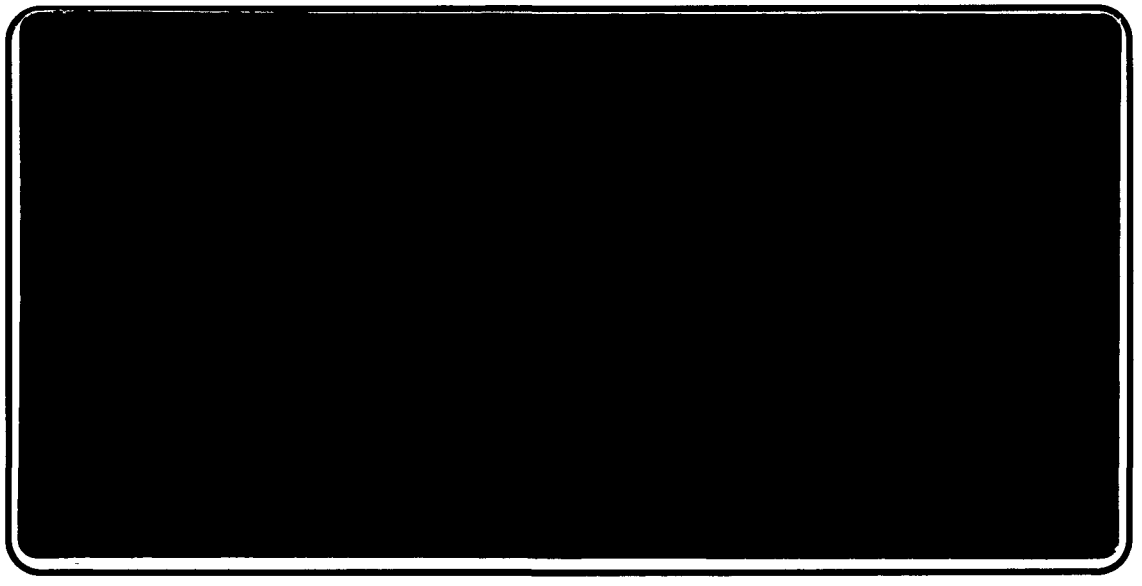

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# FACTORS AFFECTING FORMATION OF PCDD/F IN KRAFT PULP BLEACHING

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## ABSTRACT

This paper describes a laboratory study of factors that govern the formation of dioxins during the bleaching of kraft pulp. The beneficial effect of chlorine dioxide substitution was shown not to be due to a facile destruction of dioxin precursors by chlorine dioxide. A systematic study of effects of changes to the bleaching process clarified their effects, both singly and in combinations, on formation of the full range of tetra- through octachlorinated dioxins and furans. Oxygen bleaching had the greatest effect, followed by order of addition of chlorine and chlorine dioxide. The levels of all congeners were sharply reduced by introducing an oxygen stage before chlorination. Adding chlorine before chlorine dioxide decreased dioxin formation, but the effect was much smaller after an oxygen stage. Increasing chlorination temperature also had a beneficial effect, which was smaller after an oxygen stage or when chlorine was added before chlorine dioxide. Improved pulp washing and elimination of chlorination filtrate recycle did not have practically significant effects.

**KEYWORDS:** Bleaching, dioxins, effluents, chlorine, chlorine dioxide, oxygen.

## DIOXINS IN BLEACHING EFFLUENTS AND BLEACHED PULPS

Initial indications that pulp bleaching is a source of chlorinated dioxins and furans were confirmed in the United States by a cooperative industry - Environmental Protection Agency study begun in 1986 and reported in early 1988 [Amendola et al., 1989]. The latter study, conducted on effluents, sludges and pulps from five bleached kraft mills, also showed that the bleaching process was primarily responsible for dioxins formation. A contemporary investigation in Sweden [Swanson et al., 1988] confirmed the bleaching process as a source. Subsequently, unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) were found in unbleached kraft pulp and identified as precursors for the corresponding chlorinated compounds [Allen et al., 1988; LaFleur, unpublished; Voss et al., 1988; Berry et al., 1989].

A study of the effect of DBD/DBF addition and removal on the formation of a variety of chlorinated dioxin and furan congeners [LaFleur et al., 1990] provided evidence for the existence of precursors other than DBD or DBF. This study also showed that dioxins were formed almost exclusively in the chlorination stage, and virtually none found their way into the liquid phase issuing from this stage.

The "fingerprint," or relative amounts of the various congeners formed, was earlier shown [Swanson et al., 1988] to be characteristic and dominated by the 2,3,7,8 isomers of tetrachlorodibenzodioxin and tetrachlorodibenzofuran (2378-TCDD and 2378-TCDF), the former

being present in larger amounts. These observations have subsequently been confirmed and amplified by bleaching pulps that produced higher levels of dioxins and by spiking studies [LaFleur et al., 1990].

At least two studies [LaFleur et al., 1990; NCASI 591, 1990] have addressed the fate of the dioxins formed in the chlorination stage. In the laboratory, virtually all of the dioxins passed from the C-stage to the E-stage with the pulp [LaFleur et al., 1990]. The amount and composition were nearly unchanged by the E-stage, from which they emerged in both the pulp and liquid phases, in roughly equal amounts. A mill study [NCASI 591, 1990] found that most of the dioxin formed in the C-stage left the bleach plant in the E-stage filtrate and the bleached pulp.

Considerable knowledge of control methods has been gained by recent research. Kringstad and co-workers [1988] stressed the importance of keeping the ratio of the charge of chlorine (as % of o.d. pulp weight) to unbleached kappa number (chlorine multiple) below a critical value of about 0.15. Below that value, they observed no detectable dioxins, while above it there was an exponential increase in the amount of dioxins formed. They also recommended improved brownstock washing, elimination of chlorination filtrate recycle and avoiding the use of evaporator condensate for brownstock washing. Canadian researchers [Allen et al., 1988; Voss et al., 1988; and Berry et al., 1989] have confirmed the importance of the chlorine multiple, and also demonstrated beneficial effects of high chlorine dioxide substitution, careful defoamer selection, oxygen delignification, adding chlorine before chlorine dioxide, decreasing consistency and increasing pH. The success of each of these changes can be traced to a decrease in the concentration of either molecular chlorine or dioxin precursors. These studies predicted, but did not demonstrate, a detrimental effect of recycling chlorination filtrate. In addition, they failed to detect beneficial effects of increasing temperature or divided charges ("split addition") of chlorine, both of which decrease the concentration of molecular chlorine. A beneficial effect of split addition was, however, demonstrated by Hise [1989], who combined the effect with that of increased pH for dioxins control. Hise and Hintz [1989] also confirmed the importance of good brownstock washing and provided further evidence for the existence of precursors other than DBD or DBF.

With one exception [Berry et al., 1989] (where chlorine multiple and substitution were studied together), none of the studies referred to above has examined the interactions between the recommended process changes or the effect of combinations of them. Similarly, none has examined the reasons for the beneficial effect of chlorine dioxide substitution. We judged all of these issues to be in need of clarification and consequently designed a research program to address them. The results are the subject of this paper.

## EXPERIMENTAL APPROACH

The experiments consisted of laboratory simulations of the chlorination stage, followed by analysis of the resulting pulps and effluents for dioxins. In some cases, oxygen bleaching was also performed in the laboratory to determine effects on dioxins formation in the subsequent chlorination stages.

In most of the experiments, all of the tetra- through octachlorinated dibenzodioxins and dibenzofurans were determined. Isomer identifications were made at three levels of confidence, depending on whether they were based on spiking with labeled standards, by comparison of retention times with those of authentic standards, or by comparison of relative retention times with literature references or with an internally available database. A more detailed discussion of analytical methods and isomer identification criteria may be found under the heading "Experimental" below.

Chlorinations were conducted in a Quantum Technologies high-shear mixer to ensure good mixing and good control over the timing of chlorine and chlorine dioxide additions. The mixer was located in an enclosure equipped with a carbon-filtered air supply, to minimize contamination by airborne precursors and dioxins.

## EFFECT OF CHLORINE DIOXIDE ON PRECURSORS

It is now well known [Berry et al., 1989; Kringstad et al., 1988] that chlorine dioxide substitution decreases dioxin formation. In addition, laboratory studies strongly indicate that adding chlorine before chlorine dioxide gives lower dioxin levels than the reverse procedure [Berry et al., 1989]. These observations have been explained by postulating that chlorine dioxide is inert toward dioxin precursors and that chlorine converts precursors to dioxins much more slowly than it reacts with lignin. It follows that adding chlorine first results in its being rapidly consumed by lignin before it has time to generate dioxins from precursors. On the other hand, adding chlorine dioxide first satisfies a major part of the lignin's oxidant demand and thereby slows consumption of chlorine when the chlorine is finally added. As a result, an appreciable concentration of chlorine remains to serve as a driving force for reaction with dioxin precursors.

The above argument assumes that chlorine dioxide is inert toward dioxin precursors. However, this assumption is not required to enable the hypothesis to explain the observations. It may, for example, be possible that chlorine dioxide destroys dioxin precursors but fails to do so when added before chlorine simply because it is consumed by lignin before it has the opportunity.

We judged it highly desirable to learn more about the mechanism by which chlorine dioxide has its beneficial effect. Improved knowledge in this area should lead to more effective use of chlorine dioxide in dioxins control and to effective alternatives. As an initial step in this direction, we undertook experiments designed to determine whether chlorine dioxide destroys dioxin precursors. They consisted of a series of chlorinations preceded by chlorine dioxide treatment and a similar control series in which chlorine dioxide was omitted from the pretreatment. In the event of precursor destruction by chlorine dioxide, more dioxin formation is expected in the control series than in the series where the final chlorination comes after chlorine dioxide treatment.

An additional feature of these experiments was the inclusion of a prechlorination with a limited amount of chlorine in all cases. Its purpose was to satisfy much of the lignin's immediate oxidant demand and thereby minimize the chance that the chlorine dioxide would be destroyed by lignin before having the opportunity to manifest an ability to destroy precursors. The chlorine charge in this stage was chosen to be below the known threshhold value for dioxins formation [Berry et al., 1989; Kringstad et al., 1988] so that it would not consume precursors and generate a background level of dioxins, which would otherwise complicate interpretation of the results.

To summarize, these experiments took the form of three-stage chlorinations in what could be described as a (CDC) sequence. The first stage was constant for all experiments and consisted of chlorination at a chlorine multiple of 0.12. The second stage was initiated by injection of chlorine dioxide solution without intermediate filtration or washing, in an amount corresponding to an active chlorine multiple of 0.08. In the third stage, chlorine was injected to convert surviving precursors into dioxins, the determination of which served as a measure of the precursor concentration in the pulp after the chlorine dioxide treatment. In a series of control experiments, the chlorine dioxide solution was replaced by pure water.

The results of analyses of the stage 3 chlorinated pulps for 2378-TCDD, 2378-TCDF, and 1278-TCDF are summarized in Table 1. All 3 compounds showed a similar response to the experimental variables, as illustrated by the TCDD data plotted in Figure 1. The control experiments, with no

chlorine dioxide in the stage preceding final chlorination, exhibited the expected behavior: no detectable dioxin formation was observed until the total chlorine charge exceeded a threshhold value. When chlorine dioxide treatment preceded final chlorination, similar behavior was observed, with the important exception that the amounts of dioxin produced were higher.

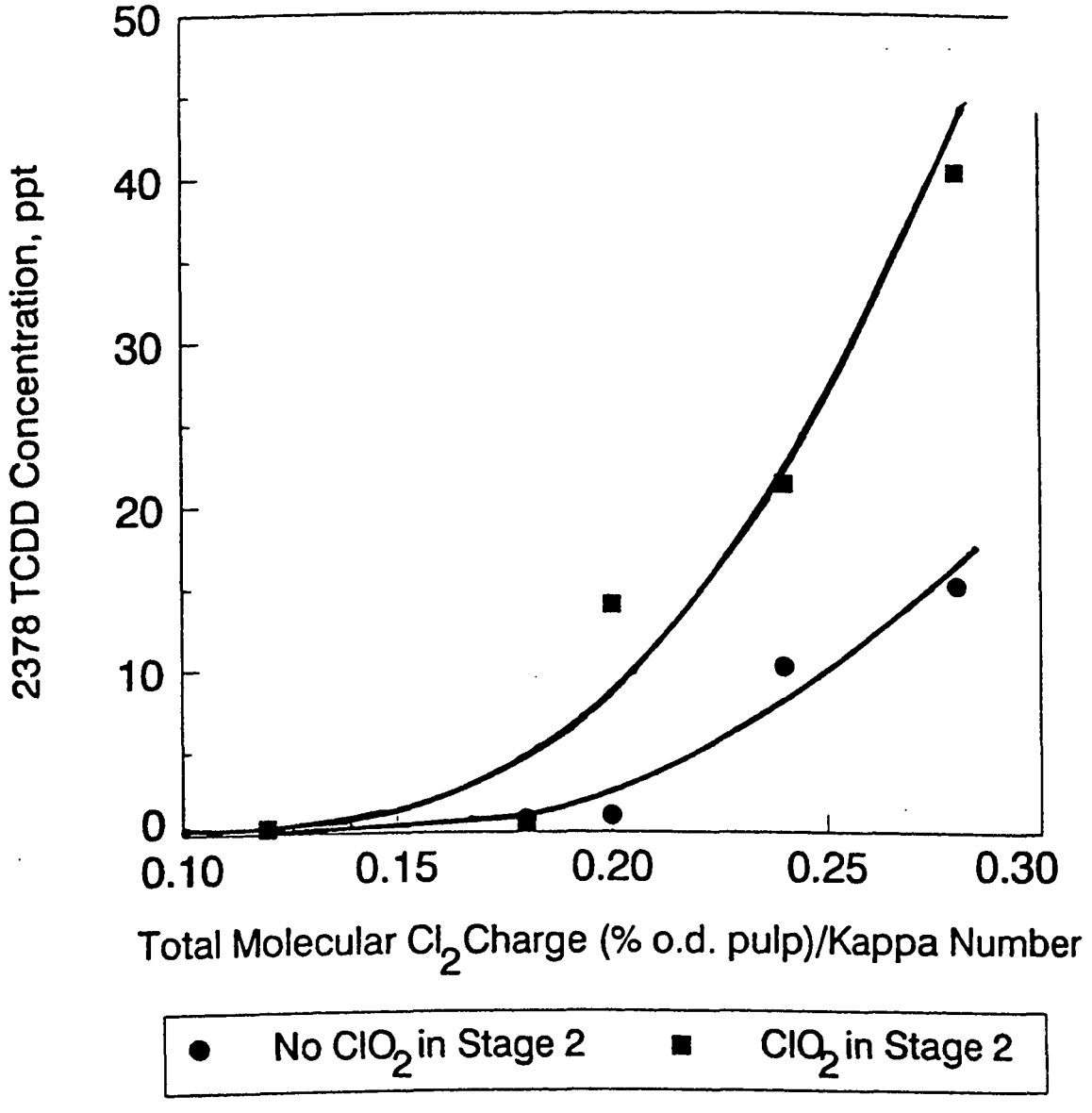


**Figure 1: Formation of 2378-TCDD in CDC Sequence**

This observation is open to three possible interpretations. One is that chlorine dioxide converts precursors to dioxins. This seems unlikely in view of the known beneficial effect of increasing substitution. Another is that it creates new precursors or liberates precursors initially chemically bound to a pulp component. The third, and perhaps most likely, is that chlorine dioxide has no effect on the precursor concentration and acts simply by reducing the oxidant demand of the lignin, leading to higher chlorine concentrations and, consequently, more efficient conversion of existing precursors in the final stage. In any case, the results show that chlorine dioxide does not readily destroy precursors, since such destruction would lead to decreased dioxin levels relative to the control experiments.

## EFFECTS OF CHLORINATION STAGE VARIABLES

Previous work in other laboratories has demonstrated that chlorination stage conditions can influence the amounts of 2378-TCDD and 2378-TCDF formed. The order of addition of chlorine and chlorine dioxide has been shown to affect TCDF formation, and preceding the chlorination stage by an oxygen stage or by improved washing has been shown to be beneficial. In addition, it has been predicted, but not demonstrated, that increasing temperature or decreasing chlorination filtrate recycle will reduce dioxins formation.

Because combinations of such changes may constitute effective and economical strategies for avoiding dioxins formation, and because knowledge of their effects is incomplete, we undertook a systematic study of effects of changes in chlorination stage variables, both singly and in combinations. The approach we adopted involved the use of a statistically designed factorial experiment and analysis of the resulting chlorinated pulps for tetra- through octachlorinated dibenzodioxins and dibenzofurans.

All chlorinations were conducted on mill softwood kraft pulp in a Quantum Technologies high shear mixer/reactor using a total active chlorine multiple of 0.25 and a chlorine dioxide substitution level of 25%. The variables and their levels were:

(A) timing of chlorine dioxide addition (15 sec before or 15 sec after chlorine),
(B) temperature (30 or 60 degrees C),
(C) chlorination stage filtrate recycle (0 or 30%),
(D) degree of oxygen delignification before the chlorination stage (0 or 40%), and
(E) degree of washing of the unbleached pulp (either near-perfect or normal, i.e., no black liquor carryover or a normal level of carryover).

The experimental design was a one-half fraction of a $2^5$ factorial. Two complete replications were done, each replication being performed on a different set of unbleached pulp samples from the same mill. The results were subjected to analysis of variance, assuming a statistical model containing main effects and two-factor interactions.

The experimental results are summarized in Table 2, and a detailed tabulation of relevant means for each important isomer is presented in Table 3. All of the isomers represented in Table 3 were detected in more than half of the samples analyzed. The results of the statistical data analysis are summarized in Table 4.

### Effect of Oxygen Bleaching

The introduction of an oxygen stage before chlorination had a greater effect than any other variable. With very few exceptions, the levels of all dioxin and furan congeners were sharply reduced by introducing the oxygen stage. The average levels of 2378-TCDD and 2378-TCDF were reduced by 88% and 82%, respectively. Only the higher dioxin (as opposed to furan) congeners were unaffected; the average level of octachlorodibenzodioxin (OCDD) formed was slightly, but not significantly, higher after oxygen bleaching.

A possibly related observation is that the reductions in chlorinated furan levels became progressively smaller with increasing chlorine substitution. This suggests that the higher congeners arise partly from precursors that are unaffected by oxygen bleaching. Since the beneficial effect of the oxygen stage is probably attributable to precursor volatilization, it is likely that nonvolatile precursors exist and possible that they are identical to the nonextractable precursors we postulated earlier. The level of the 123467/123478 HxCDF isomer pair, for example, was reduced by only 43%, and was shown earlier to be relatively unaffected by solvent extraction or by spiking with DBF.

The effect of the oxygen stage on the levels of the tetrasubstituted congeners depended on whether the chlorine dioxide was added before or after chlorine. As discussed below, adding chlorine first was effective in reducing dioxins formation. When this was done, taking the additional step of adding an oxygen stage had little or no further beneficial effect. Similarly, the effect of changing the order of addition from chlorine dioxide first to chlorine first was small after an oxygen stage. This relationship between oxygen bleaching and order of addition is exemplified by 2378-TCDD. Oxygen bleaching reduced 2378-TCDD from 4.6 to 0.4 ppt when chlorine dioxide was added first and from 1.8 to 0.4 ppt when chlorine was added first. The interaction was, in general, not observed for higher congeners, probably because they were less affected by changing the order of addition. This is another indication of a second mechanism of formation that is more important for higher congeners than lower ones.

A practical implication of the interaction between these two variables is that, because their effects are to some extent mutually exclusive, it is unlikely that incorporation of both modifications into the same sequence could be economically justified. A corollary is that, when a remedial measure is needed, it may be advisable to consider changing the order of addition before adopting the more capital-intensive oxygen bleaching alternative. As discussed below, however, the detrimental effect on delignification efficiency must also be considered.

There was a similar, but less pronounced, interaction between oxygen bleaching and temperature. Oxygen had a smaller effect on a high temperature chlorination because the temperature increase accomplished part of the reduction which could otherwise be attributed to oxygen. For example, oxygen reduced 2378-TCDF from 22 to 3 ppt in a low temperature chlorination and from 10 to 3 ppt in a high- temperature chlorination.

### Order of Addition of $Cl_2$ and $ClO_2$

Formation of 2378-TCDD and most of the tetrachlorinated furans was significantly decreased by adding chlorine before chlorine dioxide. The average levels of 2378-TCDD, 1278-TCDF and 2378-TCDF were decreased by 56%, 43% and 55%, respectively. As already mentioned, the size of the effect depended on whether an oxygen stage was present in the sequence, and it was not observed for higher congeners.

Besides depending on whether oxygen bleaching was used, this effect also depended on the degree of washing of the unbleached pulp and on the temperature of the chlorination stage. Reversing the order of addition proved to be of little value when the pulp was washed free of any residual black liquor before bleaching. For example, the average level of 2378-TCDF formed after normal mill washing was reduced from 18 to 4 ppt by adding chlorine first. The corresponding reduction after thorough removal of spent liquor was from 8 to 7 ppt. Similarly, adding chlorine first was more effective in a low-temperature chlorination than in a high- temperature stage, principally because a beneficial effect of increasing temperature made reversing the order of addition redundant.

A notable exception to the general beneficial effect of reversing the order of addition on tetrasubstituted congeners was the behavior of 2468-TCDF. In fact, this isomer is unusual in several respects. The mixing study reported above and our earlier publication [LaFleur et al., 1990] both indicate that its formation is suppressed by spiking the unbleached pulp with DBF. We also observed that its level is unaffected by prior exhaustive extraction of the unbleached pulp. These observations strongly suggest that 2468-TCDF is not formed by chlorination of DBF. It is also notable that the formation of higher congeners is not inhibited by adding chlorine first.

It should be noted that adding chlorine before chlorine dioxide gives significantly less efficient delignification than the reverse procedure. Accordingly, to achieve the same degree of delignification, a greater total charge would be required in the chlorination stage. If evaluated at a constant degree of delignification (and not at constant total active chlorine multiple, as was done in the present study) the beneficial effect of adding chlorine first would be reduced.

### Effect of Chlorination Temperature

Increasing the chlorination stage temperature from 30 to 60 degrees C decreased the amounts of 2378-TCDD, 2378-TCDF and several other chlorinated furans, most notably the 123467/123478 pair. The average reductions were 50, 49 and 40%, respectively. In contrast, the temperature increase caused an average 38% increase in the observed amount of OCDD, which may therefore be formed by a different mechanism than TCDD.

The magnitude of the temperature effect was dependent on several other variables. Its dependence on order of addition of chlorine and chlorine dioxide has already been referred to; it is typified by the behavior of total TCDF, which was reduced, on the average, from 47 to 27 ppt when chlorine dioxide was added first, but remained approximately constant at an average of 25 ppt when chlorine was added first. An interaction with oxygen has also been referred to. For example, increasing the temperature reduced the average level of 2378-TCDF from 22 to 10 ppt in the absence of oxygen, while after an oxygen stage it was roughly constant at about 3 ppt, regardless of temperature. A final, weaker interaction of the temperature effect was with recycle, which had a beneficial effect at low temperature, but not at high temperature.

### Recycling Chlorination Filtrate

The effects of chlorination filtrate recycle were generally small and were statistically significant at a high confidence level only for 2 pentachlorinated furan isomers. Their levels were slightly increased by the recycled filtrate. On the other hand, some significant interaction effects suggested that recycled filtrate may have a beneficial effect under certain conditions.

### Black Liquor Carryover

The effect of the black liquor in normally washed pulp was small and in most cases not statistically significant. It did, however, interact with the order of addition of chlorine and chlorine dioxide in the case of several TCDF's. As already described, the black liquor in the unbleached pulp increased TCDF if chlorine dioxide was added before chlorine but not if the reverse order was used.

## EXPERIMENTAL

### Effect of Chlorine Dioxide on Precursors

### Materials

Softwood kraft pulp was supplied by a north central mill. Upon receipt, the pulp was squeezed to remove dilute spent pulping liquor and washed thoroughly with distilled water. The liquor separated from the pulp before washing was stored under refrigeration for later use. The kappa number of the pulp was 31.3.

Distilled water was used for all experiments. Chlorine was research purity grade (99.99% pure) obtained from Holox. Sodium hydroxide was analytical reagent (AR) grade (98.6% pure) obtained from American Science Products. Sodium chlorate was AR grade (99.1% pure) from Baker, oxalic acid was AR grade from Mallinckrodt (99.8% pure) and the sulfuric acid was Reagent A.C.S. (98.0% pure) from Fisher.

Chlorine dioxide was generated from sodium chlorate and oxalic acid in sulfuric acid solution. Its chlorine content, expressed as a percentage of the total active chlorine, was between 0.04 and 2.60%.

## Bleaching Experiments

Bleaching experiments were conducted in a Quantum Technologies high shear mixer-reactor in a (CDC) sequence. A 120 g (o.d. basis) sample of unbleached pulp was placed in the mixer with sufficient dilution water to give a consistency of 5.5% after addition of the chlorine required for the first stage. An aqueous solution containing 3.76% chlorine (o.d. pulp basis - chlorine multiple 0.12) was placed in one of the reactor's injector reservoirs, which was then pressurized with nitrogen. The mixer was actuated, causing the chlorine solution to be injected when the rotor had attained a preset speed. Mixing was continued at 600 rpm for 10-15 sec and was repeated for 3 sec at intervals of 5 minutes. The same mixing schedule was used in the subsequent stages, described below.

After an elapsed time of 30 minutes, chlorine dioxide (0.95% based on o.d. pulp, active chlorine multiple 0.08) was injected with enough water to reduce the consistency to 4.5%. The reactor remained closed and, with the exception of a small sample of filtrate withdrawn through a sampling line, no pulp or filtrate was removed prior to injection of the chlorine dioxide. In control experiments, an equal volume of pure water was substituted for the chlorine dioxide solution.

After a further 30 minutes, and again without opening the reactor, a calculated quantity of chlorine solution was injected. Dilution water, sufficient to give a final consistency of 3.5%, was injected with the chlorine. Reaction of the chlorine with the pulp was allowed to proceed for 30 minutes, after which the reactor was opened and the filtrate sampled for pH and residual determination. The pulp was then diluted to 3% consistency, thoroughly mixed and thickened to 15% consistency. The thickened pulp was transferred to an ultraclean jar and submitted for dioxins analysis.

## Chlorination Stage Variable Effects

Several pulp samples taken from the same mill over a short time span were used for this work. The kappa number of each sample was accurately determined before bleaching and the amount of chemical to be used in the first stage of bleaching was chosen accordingly. When the first stage was chlorination, the amounts of chlorine and chlorine dioxide were chosen to give a ratio of total active chlorine to kappa number of 0.25 at a level of 25% substitution (active chlorine basis) of chlorine dioxide for chlorine. The average kappa number of the unbleached pulps was 34.

The unbleached pulp was thoroughly washed with distilled water using a fritted glass funnel. The liquor initially expressed from the pulp was reserved, and in those experiments that called for it, was added back to the pulp at a level of 6 mL/g o.d. pulp before bleaching.

The oxygen stage, if used, was carried out in the Quantum Mixer at 9% consistency with 2.0 to 3.6 % NaOH for 60 minutes at 93 deg. C. Oxygen was charged once at 100 psi. After bleaching, the pulp was removed, diluted to 4%, thickened to 20% consistency and transferred to the chlorination stage without further washing.

The chlorination stage was conducted at 4% consistency for 30 minutes at 30 or 60 deg. C. Chlorine water was iodometrically titrated, and the required volume was carefully transferred to the injector reservoir to minimize losses due to volatilization. Chlorine dioxide solution was titrated for both chlorine dioxide and chlorine and the required volume was similarly transferred to the second injector reservoir. The kappa factor was 0.25 and the level of substitution 25%. At the end of the chlorination stage the pulp was thickened to 20% consistency, sampled for dioxins analysis and transferred to the extraction stage without further washing.

Caustic extraction was conducted in the Quantum mixer with % NaOH at 0.55 times % total $Cl_2$ charge at 9% consistency and 70 degrees C for 60 min. At the end of this time, the pulp was removed, diluted to 4% consistency, and thickened to 20% consistency.

## Analytical Methods

All PCDD/F analyses were conducted on air-dried and blended pulps with 95:5 ethanol/water soxhlet extraction using the methods described earlier by NCASI [No. 551, 1989]. Modifications in spiking standards, cleanup procedures, and GC/MS acquisition parameters were adopted to accommodate the quantitation of all PCDD and PCDF isomers. Details of the sample analysis will be available in a future NCASI publication.

The $^{13}C_{12}$-labeled PCDD and PCDF internal standard spike was expanded to include all 2378-substituted isomers except 123789-HxCDD which was added at the end of sample preparations along with 1234-TCDD and 1234-TCDF for the determination of internal standard recoveries. The $^{13}C_{12}$-labeled OCDF was omitted completely due to interference in the native OCDD quantitation ions.

All GC/MS analyses were performed with a VG70-250S instrument in selected ion mode at a mass resolution of 10,000. Quantitation for TCDF isomers was conducted with a 30m x 0.25mm DB-225 column. All other PCDD and PCDF isomers were quantified with a 60m x 0.25mm DB-5 column. GC/MS acquisition parameters were consistent with those found in EPA method 1613A.

The recovery of PCDD and PCDF isomers was verified with each of the four batches of sample preparations through matrix spikes incorporating 76 individual commercially available isomers. These isomers were resolved into 60 peaks resulting in 240 determinations. The overall mean of matrix spike recoveries for all spiked isomers was 104 percent with a range of 73 to 131 percent. These results provided assurance of consistent results for most isomers.

Isomer identifications were based on three approaches providing three levels of confidence (Table 5). The best identifications were for the 2378-substituted isomers (indicated in Table 5 by underlined text). With the exception of OCDF the $^{13}C_{12}$-labeled internal and recovery standards served as exact retention time indicators in every sample. Since there is only one isomer of OCDF, the lack of a corresponding labeled standard for this analyte did not influence the level of confidence in its identification.

The second level of isomer identifications (indicated in Table 5 by **bold** text) were determined through relative retention times by reference to the relative retention times of known individual native isomer standards purchased from Cambridge Isotopes Laboratories. These isomers were used in matrix spike samples that were analyzed with each group of samples to verify expected relative retention times.

The third level of identifications were for isomers where known isomer standards were not available for confirmation (indicated in Table 5 by *italic* text). These isomer identifications were the weakest. They were based on literature references [Buser and Rappe, 1980; Bell and Gara, 1985; Hale et al., 1985; Swanson, 1988; Tiernan et al., 1989] and the relative retention times taken from observed peaks in the analysis of incinerator fly ash extracts.

## CONCLUSIONS

1. When chlorine dioxide treatment preceded chlorination, the amounts of dioxin produced were higher. These results show that chlorine dioxide does not readily destroy precursors, since such destruction would lead to decreased dioxin levels relative to the control experiments.

2. The levels of all dioxin and furan congeners were sharply reduced by introducing an oxygen stage before chlorination. The reductions in chlorinated furan levels became progressively smaller with increasing chlorine substitution. This suggests that the higher congeners arise partly from nonvolatile precursors, possibly identical to the nonextractable precursors we postulated earlier.

3. The effect of the oxygen stage on the levels of the tetrasubstituted congeners depended on whether the chlorine dioxide was added before or after chlorine. Oxygen bleaching reduced 2378-TCDD from 4.6 to 0.4 ppt when chlorine dioxide was added first and from 1.8 to 0.4 ppt when chlorine was added first. The interaction was, in general, not observed for higher congeners, probably because they were less affected by changing the order of addition. This is another indication of a second mechanism of formation that is more important for higher congeners than lower ones.

4. Formation of 2378-TCDD and most of the tetrachlorinated furans was significantly decreased by adding chlorine before chlorine dioxide while maintaining a constant total active chlorine charge. The effect depended on whether an oxygen stage was present in the sequence, and it was not observed for higher congeners. Reversing the order of addition proved to be of little value when the pulp was washed free of any residual black liquor before bleaching. Similarly, adding chlorine first was more effective in a low-temperature chlorination than in a high-temperature stage, principally because a beneficial effect of increasing temperature made reversing the order of addition redundant. Adding chlorine first decreased delignification efficiency, lessening its value as a dioxins control measure.

5. Increasing the chlorination stage temperature from 30 to 60 degrees C decreased the amounts of 2378-TCDD, 2378-TCDF and several other chlorinated furans, most notably the 123467/123478 pair. The magnitude of the temperature effect was dependent on several other variables, being smaller when chlorine was added before chlorine dioxide or when an oxygen stage preceded chlorination.

6. The effects of chlorination filtrate recycle were generally small and were statistically significant at a high confidence level only for 2 pentachlorinated furan isomers. Their levels were slightly increased by the recycled filtrate.

7. The effect of the black liquor in normally washed pulp was small and in most cases not statistically significant. The black liquor in the unbleached pulp increased TCDF if chlorine dioxide was added before chlorine but not if the reverse order was used.

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TABLE 1. DIOXIN FORMATION IN (CDC) SEQUENCE

| STAGE 2 $ClO_2$/ KAPPA | STAGE 3 $Cl_2$/ KAPPA | STAGES 1+3 CHLORINE FACTOR | STAGE 3 EXIT pH | 2378 TCDD | 2378 TCDF | 1278 TCDF |
|---|---|---|---|---|---|---|
| 0.00 | 0.00 | 0.12 | 1.6 | 0.3 | 1.7 | 1.5 |
| 0.08 | 0.00 | 0.12 | 1.5 | 0.3 | 0.6 | 0.5 |
| 0.00 | 0.06 | 0.18 | 1.4 | 0.8 | 3.5 | 2.8 |
| 0.08 | 0.06 | 0.18 | 1.4 | 0.6 | 3.1 | 2.9 |
| 0.00 | 0.08 | 0.20 | 1.4 | 1.0 | 8.7 | 6.8 |
| 0.08 | 0.08 | 0.20 | 1.3 | 13.9 | 50.3 | 24.6 |
| 0.00 | 0.12 | 0.24 | 1.4 | 10.1 | 30.3 | 14.5 |
| 0.08 | 0.12 | 0.24 | 1.4 | 21.3 | 105.5 | 49.9 |
| 0.00 | 0.16 | 0.28 | 1.3 | 15.1 | 64.2 | 28.0 |
| 0.08 | 0.16 | 0.28 | 1.2 | 40.4 | 331.9 | 152.2 |

Note: Exit pH's For stages 1 and 2 were all in the range 1.4-1.5

TABLE 2: SUMMARY OF RESULTS OF CHLORINATION VARIABLES STUDY

| $ClO_2$ DELAY | TEMP | C-STAGE FILTRATE RECYCLE | OXYGEN | BLACK LIQUOR CARRY OVER | C-STAGE EXIT pH | E-STAGE KAPPA NO. | DIOXINS AND FURANS IN CHLORINATED PULP, PPT | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 2378 TCDD | 1278 TCDF | 2378 TCDF | 12378 PeCDF | 123467/ 123478 HxCDF | TOTAL TCDD | TOTAL HxCDD | TOTAL HpCDD | OCDD | TOTAL TCDF | TOTAL PeCDF | TOTAL HxCDF | TOTAL HpCDF | OCDF |
| -1 | -1 | -1 | -1 | 1 | 1.9 | 4.0 | 8.6 | 24.6 | 49.2 | 6.6 | 14.3 | 8.8 | 0.5 | 1.9 | 5.5 | 106.2 | 19.5 | 25.0 | 7.0 | 2.4 |
| 1 | -1 | -1 | -1 | -1 | 1.9 | 4.4 | 3.3 | 6.0 | 11.9 | 1.5 | 9.2 | 3.4 | 0.5 | 1.5 | 4.9 | 33.7 | 5.9 | 14.9 | 7.0 | 1.6 |
| -1 | 1 | -1 | -1 | -1 | 2.0 | 3.7 | 1.6 | 6.4 | 6.9 | 3.8 | 3.9 | 1.8 | 0.7 | 2.2 | 5.2 | 28.9 | 12.2 | 7.2 | 1.8 | 0.5 |
| 1 | 1 | -1 | -1 | 1 | 1.8 | 5.3 | 0.6 | 4.9 | 5.7 | 3.3 | 7.8 | 0.7 | 0.5 | 2.1 | 9.1 | 26.1 | 9.9 | 13.1 | 4.4 | 1.0 |
| -1 | -1 | 1 | -1 | -1 | 1.5 | 3.9 | 4.3 | 11.0 | 21.0 | 6.8 | 13.7 | 4.5 | 0.5 | 1.3 | 3.6 | 58.4 | 19.7 | 24.0 | 4.9 | 1.2 |
| 1 | -1 | 1 | -1 | 1 | 1.4 | 5.0 | 1.6 | 6.5 | 8.0 | 5.7 | 14.2 | 1.7 | 0.5 | 1.2 | 3.5 | 33.1 | 17.3 | 24.1 | 6.8 | 1.8 |
| -1 | 1 | 1 | -1 | 1 | 1.6 | 4.7 | 4.0 | 10.6 | 14.6 | 5.2 | 7.1 | 4.2 | 0.6 | 2.1 | 5.2 | 48.9 | 17.6 | 13.4 | 4.6 | 2.4 |
| 1 | 1 | 1 | -1 | -1 | 1.8 | 5.0 | 1.9 | 9.4 | 11.1 | 8.3 | 5.7 | 2.1 | 0.6 | 1.7 | 6.5 | 45.1 | 24.0 | 11.2 | 1.5 | 0.5 |
| -1 | -1 | -1 | 1 | -1 | 2.1 | 2.5 | 0.7 | 1.8 | 2.9 | 0.6 | 5.0 | 1.0 | 0.6 | 1.8 | 4.3 | 9.1 | 2.8 | 8.1 | 4.3 | 2.5 |
| 1 | -1 | -1 | 1 | 1 | 1.9 | 3.3 | 0.3 | 1.5 | 1.5 | 1.8 | 7.0 | 0.3 | 0.4 | 1.0 | 3.8 | 10.3 | 5.9 | 11.7 | 3.1 | 0.9 |
| -1 | 1 | -1 | 1 | 1 | 2.2 | 3.4 | 0.2 | 5.6 | 5.2 | 1.8 | 2.4 | 0.3 | 0.5 | 1.4 | 5.4 | 16.6 | 6.6 | 4.1 | 2.4 | 1.2 |
| 1 | 1 | -1 | 1 | -1 | 2.0 | 3.4 | 0.4 | 3.1 | 3.0 | 2.5 | 8.1 | 0.6 | 0.5 | 1.4 | 4.9 | 17.0 | 7.8 | 12.9 | 5.4 | 1.5 |
| -1 | -1 | 1 | 1 | 1 | 1.8 | 3.0 | 0.2 | 2.1 | 2.3 | 2.5 | 7.1 | 0.4 | 0.6 | 1.3 | 5.0 | 12.6 | 7.2 | 11.9 | 3.1 | 0.8 |
| 1 | -1 | 1 | 1 | -1 | 1.9 | 3.1 | 0.4 | 3.5 | 3.7 | 2.4 | 3.8 | 0.8 | 0.8 | 2.3 | 7.5 | 17.6 | 8.0 | 6.7 | 1.9 | 0.6 |
| -1 | 1 | 1 | 1 | -1 | 1.9 | 3.0 | 0.5 | 2.9 | 2.7 | 1.5 | 3.6 | 0.6 | 0.4 | 1.6 | 6.6 | 13.1 | 5.1 | 6.3 | 2.3 | 0.9 |
| 1 | 1 | 1 | 1 | 1 | 2.0 | 3.6 | 0.4 | 1.6 | 2.2 | 1.7 | 6.4 | 0.6 | 0.6 | 2.3 | 9.2 | 12.9 | 5.8 | 11.3 | 3.5 | 0.6 |
| AVERAGES: | $ClO_2$ FIRST: | | | | 1.8 | 3.5 | 2.5 | 8.1 | 13.1 | 3.6 | 7.1 | 2.7 | 0.6 | 1.7 | 5.1 | 36.7 | 11.3 | 12.5 | 3.8 | 1.5 |
| | $Cl_2$ FIRST: | | | | 1.8 | 4.1 | 1.1 | 4.6 | 5.9 | 3.4 | 7.8 | 1.3 | 0.5 | 1.7 | 6.2 | 24.5 | 10.6 | 13.2 | 4.2 | 1.1 |
| | LOW TEMP: | | | | 1.8 | 3.6 | 2.4 | 7.1 | 12.6 | 3.5 | 9.3 | 2.6 | 0.6 | 1.5 | 4.7 | 35.1 | 10.8 | 15.8 | 4.8 | 1.5 |
| | HIGH TEMP: | | | | 1.9 | 4.0 | 1.2 | 5.6 | 6.4 | 3.5 | 5.6 | 1.4 | 0.5 | 1.8 | 6.5 | 26.1 | 11.1 | 9.9 | 3.2 | 1.1 |
| | - RECYCLE: | | | | 1.9 | 3.7 | 1.9 | 6.7 | 10.8 | 2.7 | 7.2 | 2.1 | 0.5 | 1.6 | 5.4 | 31.0 | 8.8 | 12.1 | 4.4 | 1.5 |
| | + RECYCLE: | | | | 1.7 | 3.9 | 1.7 | 5.9 | 8.2 | 4.3 | 7.7 | 1.9 | 0.6 | 1.7 | 5.9 | 30.2 | 13.1 | 13.6 | 3.6 | 1.1 |
| | - OXYGEN: | | | | 1.7 | 4.5 | 3.2 | 9.9 | 16.1 | 5.1 | 9.5 | 3.4 | 0.5 | 1.7 | 5.4 | 47.5 | 15.8 | 16.6 | 4.8 | 1.4 |
| | + OXYGEN: | | | | 1.9 | 3.2 | 0.4 | 2.8 | 2.9 | 1.8 | 5.4 | 0.6 | 0.6 | 1.6 | 5.8 | 13.7 | 6.1 | 9.1 | 3.3 | 1.1 |
| | - BLACK LIQ: | | | | 1.9 | 3.6 | 1.6 | 5.5 | 7.9 | 3.4 | 6.6 | 1.8 | 0.6 | 1.7 | 5.4 | 27.9 | 10.7 | 11.4 | 3.6 | 1.2 |
| | + BLACK LIQ: | | | | 1.8 | 4.0 | 2.0 | 7.2 | 11.1 | 3.6 | 8.3 | 2.1 | 0.5 | 1.7 | 5.8 | 33.3 | 11.2 | 14.3 | 4.4 | 1.4 |

NOTES:
1. Unbleached pulp: Mill jackpine kraft; averge kappa number 34; average viscosity 28 mPa-s.
2. $ClO_2$ was added either 15 sec before $Cl_2$ (DELAY=-1) or 15 sec after (DELAY=1).
3. Temperature was either 30 (TEMP=-1) or 60 (TEMP=1) degrees C.
4. The liquid entering the chlorination stage included either 30% recycled chlorination filtrate (RECYCLE=1) or no recycled chlorination filtrate (RECYCLE=-1).
5. The pulp entering the chlorination stage was either untreated (OXYGEN=-1) or partially delignified in an oxygen stage (OXYGEN=1, average degree of delignification 40%).
6. The brownstock was either thoroughly washed (CARRYOVER=-1) or contained carryover typical of normal mill washing (CARRYOVER=1).

TABLE 3: C-STAGE FACTORIAL EXPERIMENT MEANS FOR SIGNIFICANT EFFECTS*

| ISOMER | ISOMER NO. | GRAND MEAN | TREATMENT MEANS | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ClO, FIRST | Cl, FIRST | TEMPERATURE | | RECYCLE | | OXYGEN | | BLACK LIQUOR | |
| | | | | | LOW | HIGH | - | + | - | + | - | + |
| 2378 TCDD | 18 | 1.8 | 2.5 | 1.1 | 2.4 | 1.2 | | | 3.2 | 0.4 | | |
| OCDD | 49 | 5.6 | 5.1 | 6.2 | 4.7 | 6.5 | | | | | | |
| 1248/1346 TCDF | 59 | 1.1 | | | | | | | 1.5 | 0.6 | | |
| 2468 TCDF | 65 | 9.0 | | | | | 7.6 | 10.5 | 12.4 | 5.7 | | |
| 1278 TCDF | 71 | 6.3 | 8.1 | 4.6 | | | | | 9.9 | 2.8 | | |
| 2368 TCDF | 73 | 0.3 | 0.4 | 0.3 | | | | | 0.5 | 0.2 | | |
| 1267/1279/1469 TCDF | 76 | 0.2 | 0.3 | 0.1 | | | | | 0.3 | 0.1 | | |
| 2347 TCDF | 79 | 0.3 | | | 0.3 | 0.2 | | | 0.4 | 0.1 | | |
| 2378 TCDF | 80 | 9.5 | 13.1 | 5.9 | 12.6 | 6.4 | | | 16.1 | 2.9 | | |
| 1239/2348 TCDF | 82 | 1.5 | 1.8 | 1.1 | 2.0 | 0.9 | | | 2.6 | 0.4 | | |
| 2346 TCDF | 84 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | | | 0.2 | 0.1 | 0.1 | 0.2 |
| 2367 TCDF | 85 | 0.5 | 0.6 | 0.3 | 0.6 | 0.3 | | | 0.8 | 0.2 | | |
| 1289 TCDF | 87 | 1.8 | 2.4 | 1.3 | | | | | 2.9 | 0.7 | | |
| 12468/13468 PeCDF | 89 | 0.8 | | | | | 0.6 | 0.9 | 1.0 | 0.5 | | |
| 12368/12467/12478/13467/13478 PeCDF | 95 | 1.4 | | | | | | | 2.1 | 0.8 | | |
| 12346/12347/12469/23468 PeCDF | 103 | 0.8 | | | | | 0.7 | 1.0 | 1.2 | 0.4 | | |
| 12378 PeCDF | 105 | 3.5 | | | | | 2.7 | 4.3 | 5.1 | 1.8 | | |
| 12379/23489 PeCDF | 108 | 0.9 | | | | | | | 1.3 | 0.5 | | |
| 12369/12489/13489/23478 PeCDF | 112 | 1.2 | | | | | | | 1.7 | 0.7 | | |
| 23467 PeCDF | 113 | 2.1 | | | | | 1.6 | 2.5 | 3.0 | 1.2 | | |
| 123468 HxCDF | 116 | 0.2 | | | | | 0.2 | 0.2 | 0.3 | 0.1 | | |
| 124678/134678 HxCDF | 118 | 0.5 | | | 0.6 | 0.4 | | | 0.7 | 0.3 | | |
| 124689 HxCDF | 121 | 1.1 | | | 1.4 | 0.9 | | | 1.4 | 0.8 | | |
| 123467/123478 HxCDF | 123 | 7.5 | | | 9.3 | 5.6 | | | 9.5 | 5.4 | | |
| 123678 HxCDF | 124 | 1.0 | | | 1.2 | 0.8 | | | 1.4 | 0.7 | | |
| 123689 HxCDF | 128 | 0.3 | | | | | 0.3 | 0.4 | 0.4 | 0.2 | | |
| 123789 HxCDF | 130 | 0.2 | | | 0.3 | 0.2 | 0.2 | 0.3 | 0.3 | 0.2 | | |
| 123489 HxCDF | 131 | 2.0 | | | 2.5 | 1.6 | | | 2.7 | 1.4 | | |
| 1234789 HpCDF | 135 | 1.6 | | | 2.0 | 1.3 | | | | | | |
| TOTAL TCDD | | 2.0 | 2.7 | 1.3 | 2.6 | 1.4 | | | 3.4 | 0.6 | | |
| TOTAL TCDF | | 30.6 | 36.7 | 24.5 | 35.1 | 26.1 | | | 47.5 | 13.7 | | |
| TOTAL PeCDF | | 10.9 | | | | | 8.8 | 13.1 | 15.8 | 6.1 | | |
| TOTAL HxCDF | | 12.9 | | | 15.8 | 9.9 | | | 16.6 | 9.1 | | |
| TOTAL HpCDF | | 4.0 | | | | | | | | | | |
| OCDF | | 1.3 | | | | | | | | | | |

* All treatment means shown represent effects that are statistically significant (=>90% confidence)

TABLE 4: STATISTICALLY SIGNIFICANT EFFECTS AND 2-VARIABLE INTERACTIONS FROM C-STAGE FACTORIAL EXPERIMENT*

| ISOMER NUMBER | GRAND MEAN | A | B | C | D | E | AB | AC | AD | AE | BC | BD | BE | CD | CE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18 | 1.8 | ++ | + | | +++ | | | | ++ | + | ++ | + | | | |
| 49 | 5.6 | + | +++ | | | | | | | | | | + | +++ | |
| 59 | 1.1 | | | | +++ | | | | | ++ | | | | | |
| 65 | 9.0 | | | + | +++ | | | | | | | | | | |
| 71 | 6.3 | ++ | | | +++ | | | | + | ++ | + | | | | |
| 73 | 0.3 | ++ | | | +++ | | | | +++ | + | ++ | | | | |
| 76 | 0.2 | ++ | | | +++ | | | | + | | | ++ | | | |
| 79 | 0.3 | | +++ | | +++ | | +++ | | ++ | ++ | | +++ | | | + |
| 80 | 9.5 | +++ | ++ | | +++ | | ++ | | ++ | ++ | ++ | ++ | | | |
| 82 | 1.5 | ++ | +++ | | +++ | | ++ | | ++ | +++ | ++ | +++ | | | ++ |
| 84 | 0.2 | + | + | | +++ | ++ | | | + | | | + | | | |
| 85 | 0.5 | +++ | ++ | | +++ | | ++ | | +++ | ++ | ++ | +++ | | | ++ |
| 87 | 1.8 | + | | | +++ | | | | | + | | | | | |
| 89 | 0.8 | | | ++ | +++ | | | | ++ | | | | | | |
| 95 | 1.4 | | | | +++ | | | | | | | | | | |

* Statistical Significance:
blank: not significant
+: possibly significant (>90%,<95%)
++: significant (>95%, <99%)
+++: highly significant (>95%)

A: $ClO_2$ Delay B: Temperature C: Recycle D: Oxygen E: Black Liquor

TABLE 4(cont'd): STATISTICALLY SIGNIFICANT EFFECTS AND 2-VARIABLE INTERATIONS FROM ANALYSIS OF C-STAGE FACTORIAL EXPERIMENT*

| ISOMER NUMBER | GRAND MEAN | A | B | C | D | E | AB | AC | AD | AE | BC | BD | BE | CD | CE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 103 | 0.8 | | | ++ | +++ | | | | ++ | + | | | | | |
| 105 | 3.5 | | | + | +++ | | | | | | | | | | |
| 108 | 0.9 | | | | +++ | | | | | | | | | | |
| 112 | 1.2 | | | | +++ | | | | | | | | | | |
| 113 | 2.1 | | | + | +++ | | | | | | | | | | |
| 116 | 0.2 | | | + | +++ | | | | ++ | | | | | | |
| 118 | 0.5 | | ++ | | +++ | | | | + | | | | | | |
| 121 | 1.1 | | + | | ++ | | | | | | | + | | | |
| 123 | 7.5 | | ++ | | ++ | | | | | | | + | | | |
| 124 | 1.0 | | + | | +++ | | | | | | | | | | |
| 128 | 0.3 | | | + | +++ | | + | | | | | | | | |
| 130 | 0.2 | | ++ | + | ++ | | | | | | | | | | |
| 131 | 2.0 | | + | | ++ | | | | | | | | | | |
| 135 | 1.6 | | + | | | | | | | | | + | | | |
| TCDD | 2.0 | ++ | + | | +++ | | | | ++ | + | ++ | + | | | |
| HXCDD | 0.5 | | | | | | | + | | | | + | ++ | | |
| HpDD | 1.7 | | | | | | | | | | | | | + | |
| OCDD | 5.6 | | | | | | | | | | | | | + | |
| TCDF | 30.6 | ++ | + | | +++ | | ++ | | ++ | ++ | + | ++ | | | ++ |
| PeCDF | 10.9 | | | + | +++ | | | | | | | | | | |
| HXCDF | 12.9 | | ++ | | ++ | | | | | | | + | | | |
| HpCDF | 4.0 | | | | | | | | | | | + | | | |
| OCDF | 1.3 | | | | | | | | | | | + | | | |

* Statistical Significance: blank: not significant
+: possibly significant (>90%,<95%)
++: significant (>95%, <99%)
+++: highly significant (>95%)

TABLE 5. PCDD/F ISOMER IDENTIFICATIONS*

| | ISOMER LIST | | REL. RET. TIME | ISOMER NO. |
|---|---|---|---|---|
| DIBENZODIOXINS | | | | |
| **DB-5** | **Tetra-CDD** | **1368** | 0.820 | 1 |
| | | **1379** | 0.843 | 2 |
| | | **1369** | 0.864 | 3 |
| | | **1247/1248/1378/*1469*** | 0.911 | 7 |
| | | ***1246/1249*** | 0.925 | 9 |
| | | ***1268*** | 0.933 | 10 |
| | | ***1478*** | 0.939 | 11 |
| | | ***1279*** | 0.962 | 12 |
| | | **1234/*1236/1269*** | 0.987 | 15 |
| | | **1237/1238** | 0.994 | 17 |
| | | 2378 | 1.001 | 18 |
| | | **1239** | 1.013 | 19 |
| | | **1278** | 1.028 | 20 |
| | | **1267** | 1.044 | 21 |
| | | **1289** | 1.076 | 22 |
| **DB-5** | **Penta-CDD** | ***12468*/12479** | 0.906 | 24 |
| | | ***12469*** | 0.931 | 25 |
| | | ***12368*** | 0.945 | 26 |
| | | ***12478*** | 0.953 | 27 |
| | | ***12379*** | 0.961 | 28 |
| | | ***12369*** | 0.970 | 29 |
| | | ***12467/12489*** | 0.975 | 31 |
| | | ***12347*** | 0.985 | 32 |
| | | ***12346*** | 0.991 | 33 |
| | | 12378 | 1.001 | 34 |
| | | ***12367*** | 1.008 | 35 |
| | | **12389** | 1.024 | 36 |
| **DB-5** | **Hexa-CDD** | **124679/124689** | 0.945 | 38 |
| | | ***123468*** | 0.965 | 39 |
| | | ***123679/123689*** | 0.975 | 41 |
| | | ***123469*** | 0.980 | 42 |
| | | 123478 | 0.997 | 43 |
| | | 123678 | 1.000 | 44 |
| | | **123467/**123789 | 1.012 | 46 |
| **DB-5** | **Hepta-CDD** | **1234679** | 0.977 | 47 |
| | | 1234678 | 1.000 | 48 |
| **DB-5** | **Octa-CDD** | 12346789 | 1.000 | 49 |
| DIBENZOFURANS | | | | |
| **DB-225** | **Tetra-CDF** | **1368** | 0.685 | 50 |
| | | **1378** | 0.743 | 51 |

* Typeface indicates degree of confidence in isomer identification. See text.

TABLE 5. Continued.

| | | ISOMER LIST | REL. RET. TIME | ISOMER NO. |
|---|---|---|---|---|
| DIBENZOFURANS | | | | |
| | | **1347/1379** | 0.750 | 53 |
| | | **1247/*1468*** | 0.757 | 55 |
| | | **1367** | 0.769 | 56 |
| | | **1348** | 0.786 | 57 |
| | | **1248/1346** | 0.796 | 59 |
| | | **1237/1246** | 0.807 | 61 |
| **DB-225** | **Tetra-CDF** | ***1268*/1478** | 0.817 | 63 |
| | | **1369** | 0.820 | 64 |
| | | **2468** | 0.826 | 65 |
| | | **1238/1467** | 0.855 | 67 |
| | | ***1234*/1236/*2349*** | 0.861 | 70 |
| | | **1278** | 0.889 | 71 |
| | | **1349** | 0.897 | 72 |
| | | **2368** | 0.906 | 73 |
| | | **1267/1279/*1469*** | 0.927 | 76 |
| | | ***1249*** | 0.945 | 77 |
| | | **2467** | 0.956 | 78 |
| | | **2347** | 0.992 | 79 |
| | | 2378 | 1.002 | 80 |
| | | **1239/2348** | 1.020 | 82 |
| | | ***1269*** | 1.034 | 83 |
| | | **2346** | 1.045 | 84 |
| | | **2367** | 1.056 | 85 |
| | | **3467** | 1.127 | 86 |
| | | **1289** | 1.195 | 87 |
| **DB-5** | **Penta-CDF** | ***12468*/13468** | 0.888 | 89 |
| | | **23479** | 0.945 | 90 |
| | | ***12368*/12467/78/13467/78** | 0.953 | 95 |
| | | **13479/23469** | 0.963 | 97 |
| | | ***12479*** | 0.971 | 98 |
| | | ***13469*** | 0.975 | 99 |
| | | ***12346/47/12469/23468*** | 0.983 | 103 |
| | | **12348** | 0.997 | 104 |
| | | 12378 | 1.001 | 105 |
| | | **12367** | 1.010 | 106 |
| | | **12379/*23489*** | 1.018 | 108 |
| | | ***12369/12489/13489/*23478** | 1.043 | 112 |
| | | **23467** | 1.050 | 113 |
| | | **12349** | 1.065 | 114 |
| | | **12389** | 1.093 | 115 |
| **DB-5** | **Hexa-CDF** | **123468** | 0.957 | 116 |
| | | **124678/134678** | 0.963 | 118 |
| | | ***134679*** | 0.969 | 119 |
| | | ***124679*** | 0.976 | 120 |
| | | **124689** | 0.984 | 121 |
| | | ***123467*/123478** | 1.000 | 123 |
| | | 123678 | 1.005 | 124 |

TABLE 5. Continued.

| | ISOMER LIST | | REL. RET. TIME | ISOMER NO. |
|---|---|---|---|---|
| | DIBENZOFURANS | | | |
| | | *123479* | 1.009 | 125 |
| | | *123469/123679* | 1.019 | 127 |
| | | **123689** | 1.026 | 128 |
| | | 234678 | 1.028 | 129 |
| | | 123789 | 1.058 | 130 |
| | | **123489** | 0.885 | 131 |
| DB-5 | Hepta-CDF | 1234678 | 1.001 | 132 |
| | | *1234679* | 1.009 | 133 |
| | | *1234689* | 1.014 | 134 |
| | | 1234789 | 1.047 | 135 |
| DB-5 | Octa-CDF | 12346789 | 1.003 | 136 |